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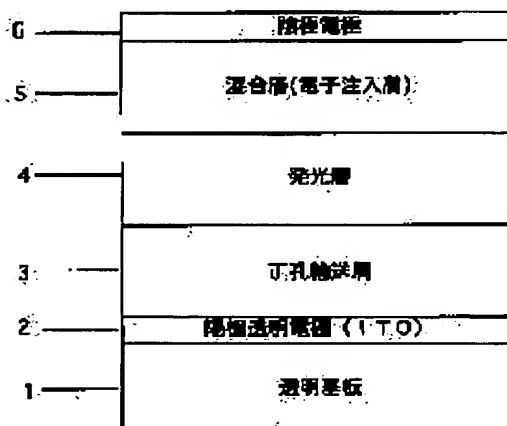
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(54) ORGANIC ELECTROLUMINESCENCE ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic electroluminescence element capable of using an inexpensive, stable metal usually used as a circuit forming material as a cathode material, with a low energy barrier in electron injection into an organic layer, low driving voltage, high efficiency, and high brightness.

SOLUTION: An organic layer coming in contact with a cathode 6 is formed with a mixture layer 5 comprising an organic metal complex compound containing at least one of an alkali metal ion, an alkali earth metal ion, and a rare earth metal ion, and an electron transport organic material, and metal capable of reducing the metal ion contained in the organic metal complex compound which is the constituting material of the mixture layer 5 into a metal in vacuum is used as a cathode material.



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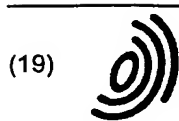
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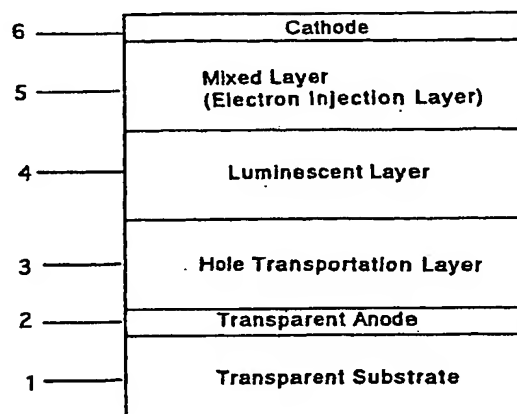
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(54) Organic electroluminescent device

(57) An organic electroluminescent (EL) device comprising at least one luminescent layer, constituted from an organic compound, between a cathode electrode and an anode electrode, the EL device further comprising an organic layer adjacent to the cathode electrode, in which the organic layer is constituted from a mixed layer of an electron-transporting organic compound and an organic metal complex compound containing at least one of alkali metal ions, alkali earth metal ions and rare earth metal ions, and the cathode electrode is constituted from a metal capable of reducing the metal ion(s) in the complex compound, in a vacuum, to the corresponding metal. The cathode electrode can be formed from a low cost and stable metal material which is conventionally used as the wiring material in the production of EL devices. The EL device ensures a diminished energy barrier in an electron injection from the cathode electrode into the luminescent layer, a lowered driving voltage, and a high efficiency and luminescence.

Fig. 1



EP 1 011 155 A2

lem with the transfer time of the dissociated ions to the close vicinity of the electrodes having a controlled velocity, thereby causing a considerable retardation of the response speed of the devices.

[0008] Moreover, in the method which includes doping the metal as a dopant in the organic layer, it is necessary to precisely control the concentration of the dopant during formation of the organic layer, because the doping concentration may affect the properties of the resulting devices.

SUMMARY OF THE INVENTION

[0009] The present invention has been made to solve the above-described problems of the prior art EL devices, and accordingly, one object of the present invention is to reduce the energy barrier in the electron injection from a cathode electrode to an organic compound layer in accordance with a simple and reliable method to thereby ensure a low driving voltage of the EL devices regardless of the work function of the cathode material.

[0010] Another object of the present invention is to provide a device (organic EL device) capable of ensuring satisfactory characteristics which are similar to, or better than, those obtained using the above-described alloy as the electrode material, even if aluminum or other low-cost stable metals which are conventionally used as the wiring material in the prior art are used solely as the cathode material.

[0011] In order to achieve the above mentioned objects, an organic electroluminescent device is provided which includes at least one luminescent layer, constituted from an organic compound, between a cathode electrode and an anode electrode opposed to the cathode electrode. The electroluminescent device further includes an organic layer adjacent to the cathode electrode, the organic layer being a mixed layer of an electron-transporting organic compound and an organic metal complex compound containing at least one member selected from the group including an alkali metal ion, an alkali earth metal ion and a rare earth metal ion. The cathode electrode includes a metal capable of reducing the metal ion(s) in the organic metal complex compound of the mixed layer, in a vacuum, to the corresponding metal.

[0012] Preferably, the mixed layer is a layer formed upon co-deposition of the organic metal complex compound and the electron-transporting organic compound.

[0013] Preferably, the metal used in the formation of the cathode electrode is any one of aluminum, zirconium, titanium, yttrium, scandium and silicon.

[0014] Preferably, the metal used in the formation of the cathode electrode is an alloy containing at least one of aluminum, zirconium, titanium, yttrium, scandium and silicon.

[0015] The above-described cathode metals and metal alloys have a high melting point, and under a vacuum, can reduce a metal ion in the organic metal complex compound to the corresponding metal.

[0016] Generally, some alkali metals, alkali earth metals and rare earth metals can exhibit a higher saturated vapor pressure than that of high-melting-point metals such as aluminum, and therefore any compound containing such alkali metals, or the like, can be reduced with the high-melting-point metals such as aluminum, silicon, zirconium and the like. For example, it is well known that calcium oxide can be reduced with aluminum to form a liberated metal calcium (cf. Chemical Handbook, "Applied Chemistry Section I", edited by the Chemical Society of Japan, Maruzen Co., p.369), and rubidium oxide and strontium oxide (cf. Metal Handbook, edited by the Japan Institute of Metals, Maruzen Co., pp.88-89) can be also reduced with aluminum to form a liberated metal rubidium and strontium, respectively.

[0017] The production of metal electrodes in the organic EL devices is carried out in a vacuum of not more than 10^{-5} Torr to deposit an atomic metal on a substrate upon melting and volatilization of the metal. Therefore, when a thermally reducible metal such as aluminum, silicon, zirconium, and the like, in an atomic state is applied onto the alkali metal compound, alkali earth metal compound or rare earth metal compound, the above-described reduction reaction in vacuum results so as to produce a reduced and liberated metal from the corresponding metal compound. In this reduction process, if the electron injection layer is constituted from a mixed layer including the organic metal complex compound and the electron transporting organic compound; the alkali metal, alkali earth metal or rare earth metal produced upon reduction and liberation of the organic metal complex compound can effectively reduce the adjacent electron transporting organic compound, thereby forming a metal doping layer.

[0018] If the alkali metal, alkali earth metal or rare earth metal compound to be reduced is an inorganic compound such as an oxide, a fluoride, and the like, it is sometimes difficult to make co-deposition of such metals with the electron transporting organic compound to form an organic layer, because the inorganic compound has a high evaporation temperature due to good stability thereof. Furthermore, due to high electrical insulation property of the inorganic compound, the remaining molecules of the inorganic compound which are unreduced may increase the driving voltage of the EL device.

[0019] In the present invention, an alkali metal, alkali earth metal or rare earth metal compound was used as the organic metal complex compound, in place of the inorganic compound thereof. The organic metal complex compound and the electron transporting organic compound were co-deposited and mixed to form a mixed layer. The produced mixed layer was further coated with a cathode electrode made of a specific electrode material which contains a metal capable of reducing, in a vacuum, the metal ion(s) contained in the organic metal complex compound. Thus, based on

thracene, naphthacene and phenanthrene, as well as derivatives thereof; condensed heterocyclic compounds such as phenanthroline, bathophenanthroline, phenanthridine, acridine, quinoline, quinoxaline, phenazine and the like as well, as derivatives thereof; and fluoreceine, perylene, phthaloperylene, naphthaloperylene, perynone, phthaloperynone, naphthaloperynone, diphenylbutadiene, tetraphenylbutadiene, oxadiazole, aldazine, bisbenzoxazoline, bisstyryl, pyrazine, cyclopentadiene, oxine, aminoquinoline, imine, diphenylethylene, vinylanthracene, diaminocarbazole, pyrane, thiopyrane, polymethine, merocyanine, quinacridone and rubrene, as well as derivatives thereof.

[0027] In addition to these organic compounds, metal-chelated complex compounds described in Japanese Unexamined Patent Publication (Kokai) Nos. 63-295695, 8-22557, 8-81472, 5-9470 and 5-17764 can be appropriately used as the organic compounds. Among these metal-chelated complex compounds, metal-chelated oxanoid compounds, for example, metal complexes which contain, as a ligand thereof, at least one member selected from 8-quinolinolato such as tris(8-quinolinolato)aluminum, bis(8-quinolinolato)magnesium, bis[benzo(f)-8-quinolinolato]zinc, bis(2-methyl-8-quinolinolato)aluminum, tri(8-quinolinolato)indium, tris(5-methyl-8-quinolinolato) aluminum, 8-quinolinolatolithium, tris(5-chloro-8-quinolinolato)gallium and bis(5-chloro-8-quinolinolato) calcium, as well as derivatives thereof, can be appropriately used.

[0028] Furthermore, oxadiazoles disclosed in Japanese Patent Kokai Nos. 5-202011, 7-179394, 7-278124 and 7-228579, triazines disclosed in Japanese Patent Kokai No. 7-157473, stilbene derivatives and distyrylarylene derivatives disclosed in Japanese Patent Kokai No. 6-203963, styryl derivatives disclosed in Japanese Patent Kokai Nos. 6-132080 and 6-88072, and diolefin derivatives disclosed in Japanese Patent Kokai Nos. 6-100857 and 6-207170 are preferably used in the formation of the luminescent layer and the electron transportation layer.

[0029] Furthermore, a fluorescent whitening agent such as benzoxazoles, benzothiazoles and benzoimidazoles can be used as the organic compounds, and includes, for example, those described in Japanese Patent Kokai No. 59-194393. Typical examples of the fluorescent whitening agent include the fluorescent whitening agents classified under the group of benzoxazoles such as 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)-1,3,4-thiadiazole, 4,4'-bis(5,7-t-pentyl-2-benzoxazolyl)stilbene, 4,4'-bis[5,7-di(2-methyl-2-butyl)-2-benzoxazolyl]stilbene, 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)thiophene, 2,5-bis[5-(α , α -dimethylbenzyl)-2-benzoxazolyl]thiophene, 2,5-bis[5,7-di(2-methyl-2-butyl)-2-benzoxazolyl]-3,4-diphenylthiophene, 2,5-bis(5-methyl-2-benzoxazolyl)thiophene, 4,4'-bis(2-benzoxazolyl)biphenyl, 5-methyl-2-{2-[4-(5-methyl-2-benzoxazolyl)phenyl]vinyl} benzoxazole and 2-[2-(4-chlorophenyl)vinyl]naphtho(1,2-d)oxazole; under the group of benzothiazoles such as 2,2'-(p-phenylenedipynylene)-bisbenzothiazole; and under the group of benzoimidazoles such as 2-{2-[4-(2-benzoimidazolyl)phenyl]vinyl} benzoimidazole and 2-[2-(4-carboxyphenyl)vinyl]benzoimidazole.

[0030] As the distyrylbenzene compound, the compounds disclosed in European Patent No. 373,582 can be used, for example. Typical examples of the distyrylbenzene compound include 1,4-bis(2-methylstyryl)benzene, 1,4-bis(3-methylstyryl)benzene, 1,4-bis(4-methylstyryl)benzene, distyrylbenzene, 1,4-bis(2-ethylstyryl)benzene, 1,4-bis(3-ethylstyryl)benzene, 1,4-bis(2-methylstyryl)-2-methylbenzene and 1,4-bis(2-methylstyryl)-2-ethylbenzene.

[0031] Furthermore, distyrylpyrazine derivatives disclosed in Japanese Patent Kokai No. 2-252793 may also be used in the formation of the luminescent layer and the electron transportation layer. Typical examples of the distyrylpyrazine derivatives include 2,5-bis(4-methylstyryl) pyrazine, 2,5-bis(4-ethylstyryl)pyrazine, 2,5-bis[2-(1-naphthyl)vinyl]pyrazine, 2,5-bis(4-methoxystyryl)pyrazine, 2,5-bis[2-(4-biphenyl)vinyl]pyrazine and 2,5-bis[2-(1-pyrenyl)vinyl]pyrazine.

[0032] In addition, dimethyldiene derivatives disclosed in European Patent No. 388,768 and Japanese Patent Kokai No. 3-231970 can also be used as the material of the luminescent layer and the electron transportation layer. Typical examples of the dimethyldiene derivatives include 1,4-phenylenedimethyldiene, 4,4'-phenylenedimethyldiene, 2,5-xylylenedimethyldiene, 2,6-naphthylenedimethyldiene, 1,4-biphenylenedimethyldiene, 1,4-p-terphenylenedimethyldiene, 9,10-anthracenediyl dimethyldiene, 4,4'-(2,2-di-t-butylphenyl vinyl)biphenyl and 4,4'-(2,2-diphenylvinyl)biphenyl, as well as derivatives thereof; silanamine derivatives disclosed in Japanese Patent Kokai Nos. 6-49079 and 6-293778; polyfunctional styryl compounds disclosed in Japanese Patent Kokai Nos. 6-279322 and 6-279323; oxadiazole derivatives disclosed in Japanese Patent Kokai Nos. 6-107648 and 6-92947; anthracene compounds disclosed in Japanese Patent Kokai No. 6-206865; oxynate derivatives disclosed in Japanese Patent Kokai No. 6-145146; tetraphenylbutadiene compounds disclosed in Japanese Patent Kokai No. 4-96990; and organic trifunctional compounds disclosed in Japanese Patent Kokai No. 3-296595; as well as coumarin derivatives disclosed in Japanese Patent Kokai No. 2-191694; perylene derivatives disclosed in Japanese Patent Kokai No. 2-196885; naphthalene derivatives disclosed in Japanese Patent Kokai No. 2-255789; phthaloperynone derivatives disclosed in Japanese Patent Kokai Nos. 2-289676 and 2-88689; and styrylamine derivatives disclosed in Japanese Patent Kokai No. 2-250292.

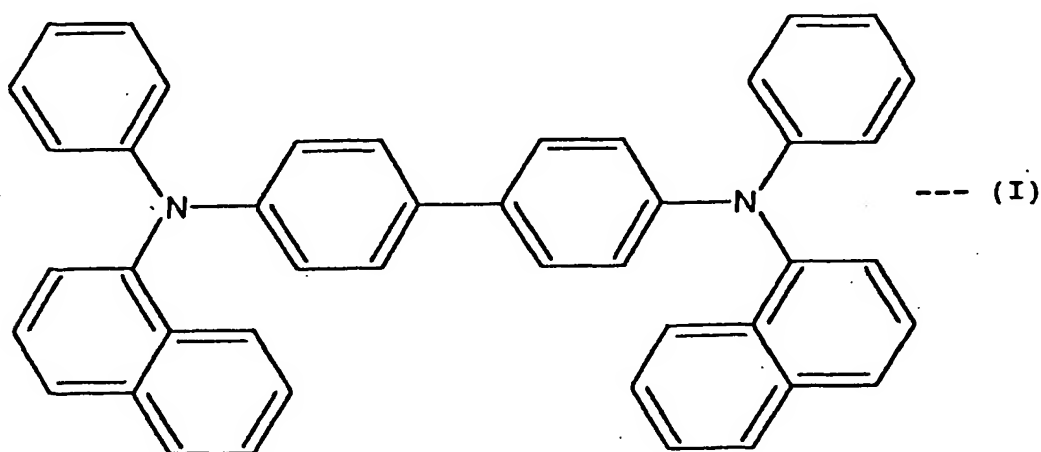
[0033] Moreover, any well-known compounds which are conventional in the production of the prior art organic EL devices can be appropriately used as the organic compound in the production of the organic EL device of the present invention.

[0034] The arylamine compounds used in the formation of the hole injection layer, the hole transportation layer and the hole-transporting luminescent layer, although they are not restricted thereto, preferably include those disclosed in Japanese Patent Kokai Nos. 6-25659, 6-203963, 6-215874, 7-145116, 7-224012, 7-157473, 8-48656, 7-126226, 7-

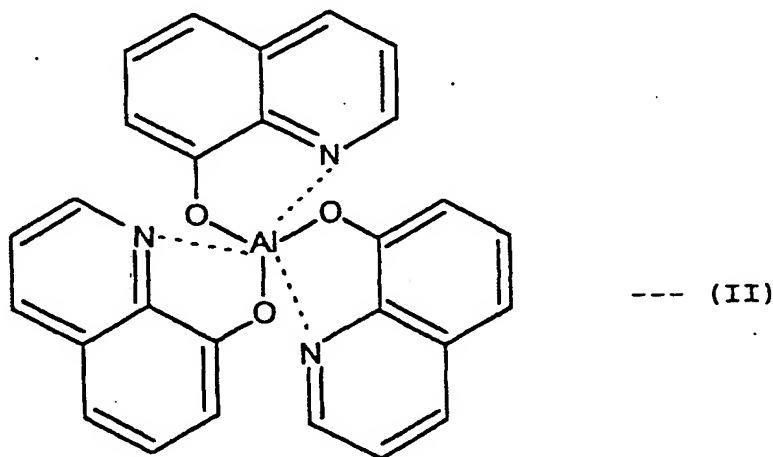
Example 1:

[0041] The organic EL device having the lamination structure illustrated in Fig. 1 was produced according to the present invention.

[0042] A glass substrate 1 was coated with an ITO (indium-tin oxide) layer having a sheet resistance of $25 \Omega/\square$, commercially available as a sputtering deposition product from Sanyo Shinku Co., to form a transparent anode electrode 2. Alpha (α)-NPD having a hole transporting property, represented by the following formula (I), was deposited onto the ITO-coated glass substrate 1 under the vacuum vapor deposition conditions of 10^{-6} Torr and $2 \text{ \AA}/\text{sec}$ to form a hole transportation layer 3 having a thickness of 500 \AA .



[0043] Thereafter, an aluminum complex of tris(8-quinolinolato) (hereinafter, referred to as "Alq") capable of exhibiting a green luminescence, represented by the following formula (II), was deposited onto the hole transportation layer 3 under the same vacuum vapor deposition conditions as in the above-described deposition of the hole transportation layer 3 to form a luminescent layer 4 having a thickness of 650 \AA .



[0044] After the formation of the luminescent layer 4, to form an electron injection layer 5 in the form of a mixed layer, a lithium complex of mono(8-quinolinolato) (referred to as "Liq", as an organic metal complex compound) represented by the following formula (III) and Alq (as an electron-transporting organic compound) in a molar ratio of 1 : 1 (Liq : Alq) were co-deposited under the pressure of 10^{-6} Torr onto the luminescent layer 4. The electron injection layer 5 hav-

obtained in Example 2.

Comparative Example 2:

[0053] The procedure of Example 2 was repeated to produce an organic EL device with the proviso that, for the purpose of comparison, an electron injection layer was formed from the inorganic compound, lithium fluoride (LiF) and the electron-transporting organic compound (Alq). That is, α -NPD was first deposited onto the ITO-coated glass substrate to form a hole transportation layer having a thickness of 500 Å, followed by vacuum deposition of Alq to form a luminescent layer having a thickness of 400 Å. Thereafter, lithium fluoride (LiF) and the electron-transporting organic compound (Alq) in a molar ratio of 1 : 1 (LiF : Alq) were co-deposited to form an electron injection layer (mixed layer) having a thickness of 300 Å. After the formation of the electron injection layer, aluminum (Al) was deposited at a thickness of 1,000 Å over the electron injection layer to form a cathode electrode.

[0054] In the produced organic EL device, as is plotted with black dots in Fig. 3, only maximum luminance of 7,300 cd/m² was obtained at the applied bias voltage of 17 volts, and the applied bias voltage of 15.5 volts was required to obtain a luminance of 1,000cd/m².

[0055] The comparison of the above results with those of Example 2 indicates that an electrically insulating inorganic compound such as LiF can remarkably deteriorate the luminance property of the EL device, in contrast to the organic metal complex compound, due to the unreduced LiF being retained in the electron injection layer (mixed layer).

[0056] Although the invention has been described with reference to particular means, materials and embodiments, it is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the claims.

Claims

1. An organic electroluminescent device comprising at least one luminescent layer, constituted from an organic compound, between a cathode electrode and an anode electrode opposed to said cathode electrode; wherein:

said electroluminescent device further comprises an organic layer adjacent to said cathode electrode, said organic layer being a mixed layer of an electron-transporting organic compound and an organic metal complex compound containing at least one member selected from the group comprising an alkali metal ion, an alkali earth metal ion and a rare earth metal ion; and

said cathode electrode comprising a metal capable of reducing the metal ion(s) in said organic metal complex compound of said mixed layer, in a vacuum, to the corresponding metal.

2. The organic electroluminescent device according to claim 1, in which said mixed layer is a layer formed upon co-deposition of said organic metal complex compound and said electron-transporting organic compound.

3. The organic electroluminescent device according to claim 1 or 2, in which the metal used in the formation of said cathode electrode is any one of aluminum, zirconium, titanium, yttrium, scandium and silicon.

4. The organic electroluminescent device according to claim 1 or 2, in which the metal used in the formation of said cathode electrode is an alloy containing at least one of aluminum, zirconium, titanium, yttrium, scandium and silicon.

Fig. 2

